IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the PATENT application of

Mark S. F. CLARKE et al.

Group Art Unit: 1754

Serial No: 09/932,986

Examiner: LISH, P.

Filed: August 21, 2001

For: PRODUCTION OF STABLE AQUEOUS DISPERSIONS OF CARBON NANOTUBES

DECLARATION UNDER 37 C.F.R. § 1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

DANIEL L. FEEBACK declares that:

1. I am a co-inventor of the invention entitled "PRODUCTION OF STABLE AQUEOUS DISPERSIONS OF CARBON NANOTUBES", disclosed and claimed in the above-identified patent application.

2. Prior to March 6, 2001, Mark S.F. Clarke and I had conceived and reduced to practice the invention of isolating single walled carbon nanotube structures embedded within raw material utilizing at least methyl-β-cyclodextrin.

3. Evidence of our conception and reduction to practice of the invention is provided herewith in the form of attached copies of two pages from a laboratory notebook prepared by Mark S.F. Clarke. The laboratory notebook, including the pages attached hereto, was prepared prior to March 6, 2001 and includes the results of tests

conducted prior to March 6, 2001 and relating to the successful isolation and dispersion of single walled carbon nanotube structures in methyl-β-cyclodextrin (referred to as MBC in the attached laboratory notebook pages).

3. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 5/27/2003 By: _____

Daniel L. Feeback

[redacted]

Nanotube Production

RESULTS TO DATE:

Using purified laser nanotubes (from Brad/Olga – Batch #27 ??) we have been able to successfully isolate long (i.e. 5-10 um's long) nanotubes from this material using 50mg/ml MBC dispersion. Using TEM, we have found that these long nanotubes are in the 10,000xg pellet (microfuge tube, 1ml volume) and that the pellet can be washed by 10,000xg centrifugation up to 3 times with 1 ml of water and still have clean, long nanotubes in the pellet soluble in water. In the TEM preparation (drying down onto carbon mesh) we observed large highly organized rafts of nanotubes oriented in parallel with each other indicating that as the water evaporated/dried off the tubes came together in a non-random fashion which appeared to achieve the least surface contact between tubes (Sample F2-9). This indicated that the tubes existed in solution as single SWCNT as they appear to want to repel each other. There was very little contaminating material in the sample with no material stuck between the tubes in the rafts in the TEM. When this sample (M4 – washed F2-9 – see keys [redacted]) was dried down onto Carbowax PEG 200 coated glass coverslips for AFM ([redacted]) the following was observed. Single SWCNT's attached to Carbowax 200 surface if neat solution of M4 was incubated overnight and allowed to dry. The Carbowax appeared to coat the single SWCNT as "bead-like" spots along the tubes. The Carbowax coating was not a very even coating and junk (maybe coiled tubes) had come together were a lot of Carbowax was still attached to the surface. In the case of 1:10, 1:100 and 1:1000 dilutions of M4 on Carbowax surfaces it appeared as if no Carbowax remained on the surface of the coverslip, leaving "raft-like" fibers of SWCNT attached to the surface after overnight drying, structures very reminiscent of the "rafts" seen in the TEM.

EXPERIMENTAL PLAN

Prepare more suspended single SWCNT using purified laser tubes (#27 batch from Brad/Olga). Also prepare from unpurified laser tubes (#36 –60H2).

Purified Laser Tubes – resuspended at 1mg/ml in 50mg/ml MBC (D2O) in 1.8 ml spin tubes, total of 3 ml prepared in 1.5 ml aliquots. Sample shaken on vortexed for 30 min at RT. Spun at 100xg for 5 min to remove heavy particulate matter. Supernatant (approx. total of 2.5 ml removed and separated on DeSalt column (Pierce) using water and 1ml application volume (total of 2.6ml applied to column). 1ml fractions collected and 100ul aliquots read at 450nm for %T. Fractions #3 – 11 centrifuged at 10,000xg for 10 min, 900 ul of supernatant removed and pellets pooled together in remaining volume (i.e. 1.1 ml). Sample again centrifuged at 10,000xg for 10 min, 750ul of supernatant removed and pellet washed twice more with 1 ml of clean ddH2O. Pellet resuspended in 1 ml of ddH2O. Sample given ID of F3-11/P4. A similar scheme was followed for unpurified laser nanotubes (3mg dry weight Laser #36 suspended in 50mg/ml MBC, 20 sec at 23,000 rpm homogenizer, 100xg spin, remove supernatant) except that total sample volume (100xg supernatant) applied to the column volume was 800 ul of supernatant plus 200 ul of ddH2O. Fractions #2 –10 were pooled, centrifuged at 10,000xg, 900 ul of supernatant removed and the remaining pellets combined and centrifuged. The mixtured was then centrifuged again and 750ul of supernatant removed. The sample was then washed twice more with ddH2O (1ml volume) by centrifugation at 10,000xg. The remaining pellet was suspended in 500 ul of ddH2O and given a Sample ID of UPL1.

Also, 1mg/ml of purified laser SWCNT (from Brad/Olga – Batch #27 ?? in water) made up in 50mg/ml (aq) of 2-hydropropyl-β-cyclodextrin (2HPBC) was vortexed for 30 min, centrifuged at 100xg for 5 min, supernatant passed through a 0.2um RC filter (15mm diameter, 1ml syringe – filtration removed the vast majority of color from the solution, probably due to caking of the filter) and then centrifuged at 10,000xg to form a pellet. This pellet was then washed 2 times with 1 ml volumes of ddH2O as above. The final pellet was resuspended in 0.1 ml of ddH2O and given a Sample ID of LP2H1. (this sample pelleted better with no streaking down the side of the tube??).

TEM RESULTS ([redacted])

Sample F3-11/P4 contained lots of nanotubes arranged as rafts as before. Sample T/M (a mix of MBC and Tau Acid – Sample M4 diluted to a final concentration of 0.12mM Tau Acid and then washed by centrifugation) showed raft morphology as well. If the Tau Acid substituted into the MBC layer the nanotubes will have a net negative surface charge. Check this with AFM on amino-surface. LP2H1 (2 hydroxypropyl B cyclodextrin) suspended tubes contained very few tubes but those that were there appeared to a have a raft appearance. Repeat solubilization using 2HPBC and purified on column rather than by filtering through a 0.2um filter. UPL1 sample was relatively dirty and but there were alot of tubes in it. It was not however apparent that the tubes had been seperated from ordered ropes by MBC solubilization and that they had come back together as rafts as they appeared to more than 1 or 2 layers thick.

Preparation of 2HPBC Suspended Tubes ([redacted])

1ml of a 2mg/ml LP (#27 batch aq stock) diluted to 500mg/ml CNT in 50mg/ml 2HPBC (total volume 4ml), vortexed for 30 min and spun at 100xg. Supernatant removed and pellet again extracted with 3 ml of 50 mg/ml 2HPBC, vortexed for 30 min and spun at 100xg. Supernatant added to first supernatant (final volume of 7 ml). Solution left overnight, revortexed for 30 min at RT, spun at 100xg and supernatant (total volume of 6.8 ml) collected for column separation. Supernatant volume adjusted to 7 ml total with ddH2O and added to a water equilibrated DeSalt Column (5000 MW cut-off). 1 ml fractions collected and 100ul aliquots read for %T at 450nm. Fractions 4 – 13 pooled, centrifuged at 10,000xg and pellets pooled and split into two equal volumes. These samples were then centrifuged at 10,000xg and supernatant removed. Color was left in the 10,000xg supernatant so supernatant was collected for checking by TEM for CNT's. The pellet was the washed with ddH2O by centrifugation a total of 2 more times. The final pellets were then each resuspended in 0.5ml of ddH2O. One suspension was exposed to a magnet for 20 min, supernatant removed and given the sample ID 2HPBC-MSS. The magnetic material was resuspended in 0.5ml of ddH2O and given the sample ID 2HPBC-MSP. The untreated suspension was given the ID 2HPBC.

Sample UPL1 contained a lot of metal catalyst particles. Took a 200 ul volume of original UPL1 sample and placed it in 1.8ml conical microfuge tube and exposed it to the Dynabead single magnet. After 20 min a black deposit formed on the wall of the tube leaving a grey solution. Collected the grey solution (Sample ID as UPL1-MSS) and then resuspended the black magnetic material in 200 ul of water (Sample ID as UPL1-MSP). Will check equal volumes of all three samples (i.e. UPL1, UPL1-MSS and UPL1-MSP) for metal particles by TEM.

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